a detailed explanation of this phenomenon is one of the goals of this research.

G. A. Doorakian, H. H. Freedman
The Dow Chemical Company, Eastern Research Laboratory
Wayland, Massachusetts 01778
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The Resistance of Radon to Oxidation in Aqueous Solution[1]

Sir:

Haseltine and Moser[2] have reported the oxidation of radon in aqueous solution. We have recently attempted to duplicate their results, and on the basis of more than 60 experiments we have become convinced that their conclusions are incorrect.

In their most convincing result, Haseltine and Moser found that when a solution 10^{-7} M in $^{226}RaBr_2$ and 0.1 M in $K_2S_2O_8$ was allowed to stand for 23 days, most of the ^{222}Rn formed could not be extracted into hexane and could not be volatilized by bubbling a gas through the solution.

We have repeated this experiment using $^{226}RaCl_2$ solutions, but otherwise duplicating the conditions of Haseltine and Moser. We found that less than 6% of the radon remained in the 23-day old persulfate solution after argon had been bubbled through it for 3 hr, or after it had been extracted with an equal volume of hexane. On the other hand, after the solution had stood for 38–39 days, 80% of the radon could not be volatilized by argon bubbling, and two-thirds of it did not extract into an equal volume of hexane. This radon could, however, be removed from solution by centrifuging in a clinical centrifuge. After the supernatant solution was withdrawn, the radon activity in the residue increased with time. This indicated that the residue contained radium, with which the radon had not yet reached equilibrium.

We have attempted to oxidize radon in the same way with the other reagents tried by Haseltine and Moser, and also with ozone and with sodium perxenate. In no case was a solution obtained from which the radon could not be removed either by bubbling in argon or by centrifuging; and whenever the radon was removed by centrifugation, it was accompanied by radium in excess of the equilibrium amount. It is noteworthy that even from some $RaCl_2$ solutions containing no other reagents, significant portions of the radon could not be volatilized, but could be removed by centrifugation.

We conclude from these studies that the phenomena observed by Haseltine and Moser do not result from oxidation of radon. They seem instead to be brought about by the precipitation of some or all of the radium by reagents or impurities in the solutions. (The sulfate that gradually builds up in persulfate solutions is one likely cause of such precipitation.) The radon that forms within the precipitate is mechanically trapped and will neither extract into hexane nor volatilize in a gas stream.

We have found no evidence for the existence of radon compounds in aqueous solution, and we hope that others will undertake to verify our conclusions.

Kathleen Flohr, Evan H. Appelman
Argonne National Laboratory
Argonne, Illinois 60439
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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. W. Haseltine and H. C. Moser, *J. Am. Chem. Soc.*, **89**, 2497 (1967).

Rapid Time Scale for Hydrogen-Atom Abstraction by Recoil Tritium Atoms. Nonequilibrium Allyl Radicals from Propylene

Sir:

We have measured the HT yield from the recoil tritium abstraction reaction with the CH_3 group of propylene, as in (1), and have compared it to the well-established correlation of hydrocarbon bond dissociation energies with such hydrogen abstraction yields.[1–6] The discrepancy between this apparent value for the allyl–H bond dissociation energy (93 kcal/mole) and the measured values by other well-established techniques (87.8 kcal/mole)[7] leads us to the conclusion that the equilibrium bond dissociation energy is not appropriate for such a comparison in this particular situation. We believe that the lower yield characteristic of a stronger bond reflects the fact that the transfer of the hydrogen atom from C_3H_5–H bonding to the T–H bonding is completed while the bond lengths (and perhaps the angles) of the C_3H_5 residue still differ substantially from those of an allyl radical in its equilibrium configuration.

$$T^* + CH_3{-}CH{=}CH_2 \longrightarrow HT + CH_2{-}CH{=}CH_2 \qquad (1)$$

The largest geometrical differences between propylene and allyl involve the C–C distances and the C–C–C bond angle. Failure to attain the equilibrium allylic configuration during H-atom transfer is thus essentially equivalent to very high vibrational excitation of the C–C stretching and C–C–C bending vibrations of the allyl radical, and represents relaxation energy not yet totally available for "loosening" of the C–H bond at the time of atom transfer. Since the C_1–C_2 and C_2–C_3 bond distances are 1.336 and 1.501 Å, respectively, in propylene,[8] and about 1.40–1.44 Å in the equilibrium allyl radical,[9] the chief geometrical deformation in terms of energy involves deviations in C–C bond distances as much as 0.1 Å.

We conclude that the time scale for the hydrogen-abstraction reaction is definitely shorter than that required for complete adjustment of geometric relationships to those of the thermally equilibrated allyl radical. By assuming that the time required for 0.1-Å adjust-

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(6) All HT yields are expressed as yields per C–H bond under equivalent conditions of exposure to energetic tritium atoms.

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(9) C. L. Currie and D. A. Ramsay, *ibid.*, **45**, 488 (1966).